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Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference

JEO/559

2. Patent application number
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0402963.3 — 11 FEB 2004

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

THE UNIVERSITY OF NOTTINGHAM
UNIVERSITY PARK
NOTTINGHAM
NG7 2RD

Patents ADP number *(if you know it)* 437692700 2.

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

COUNTER CURRENT MIXING DEVICE FOR TWO DIFFERENT FLUIDS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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7442494002

Patents ADP number *(if you know it)* (Si/07 10/2/05)

6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
N/A		

7. Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)

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8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request?

NO

Answer YES if:
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
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Otherwise answer NO (See note d)

9. Accompanying documents: A patent application must include a description of the invention. Not counting duplicates, please enter the number of pages of each item accompanying this form:

	Continuation sheets of this form	
8	Description	~~2~~
4 2	Claim(s)	~~2~~
1	Abstract	~~2~~
37 3	Drawing(s)	

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	✓
Request for a preliminary examination and search (Patents Form 9/77)	
Request for a substantive examination (Patents Form 10/77)	
Any other documents (please specify)	1 PAGE of references

11. I/We request the grant of a patent on the basis of this application.

Signature(s) [signature] Paul Cartledge, Head of Research Grants & Contracts, Research Support Office

Date 19th Feb 04

12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

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Counter current mixing device for two different fluids

Field of the Invention

The invention is a device enabling the efficient mixing of two streams of fluid of widely differing densities. More specifically, one stream is of a near-critical or supercritical fluid whilst the other is of a denser aqueous solution. Most preferably, one stream is of supercritical H_2O, and the other is of a metal salt solution. Most preferably, the invention can be used in the continuous synthesis of nanoparticles of metal oxides in high temperature H_2O without the blockages and inhomogenaities in particle size and shape that are associated with other designs of mixer.

Background

Metal oxide particles with nanometer scale dimensions have a wide range of uses, including (but not limited to) catalysts, pigments, polishes, ultraviolet absorbers and in ceramics. It is well known that metal oxide particles can be formed by chemical reaction of aqueous solutions of metal salts with near or supercritical water. In principle, this methodology offers distinct advantages over other methods of nanoparticle creation in terms of cost and viability as it allows the reaction to be performed as a continuous process. However it is difficult to perform this reaction on a commercial scale utilising current methods because existing reactor configurations do not allow the precipitation reaction to be controlled leading to frequent blockage of the reactor and inadequate control of particle size and shape. Hence within this process, the design of the reactor where the supercritical H_2O and the salt solution mix is of critical importance to the size and properties of the nanoparticles produced.

This invention details a more efficient and versatile method of producing a range of transition metal oxide nanoparticles that could be catalytically active, and thus it possesses obvious industrial applicability.

Particle size can be important for catalytic processes and other uses, and is dependant on the nature of the metal and also the intended application. For example commercially produced Cerium Oxide (from Johnson Matthey) has a surface area of $250m^2/g$ whereas silver particulate with a surface area of $60\text{-}100m^2/g$ can be commercially viable. The funnel, without optimisation or devoted work on CeO_2, has produced particulates with surface areas of $100m^2/g$. This can be improved considerably with additional work focussed on lowering the particle sizes produced by adjusting the operating conditions and metal salt concentrations.

Whilst the surface area of a catalyst is very important, the physical nature of the particles can also determine their success in the intended application. For example, zirconium oxide nanoparticulates are often amorphous in structure, which is not an appropriate form for many catalytic applications. The funnel reactor has prepared crystalline ZrO_2, which is much more useful.

Supercritical fluids, and particularly supercritical water, have been used to produce metal nanoparticles (Adschiri, Kanazawa et al. 1992; Adschiri, Hakuta et al. 2000; Galkin, Kostyuk et al. 2000; Adschiri, Hakuta et al. 2001; Cabanas, Darr et al. 2001; Cote, Teja et al. 2002; Hao and Teja 2003; Viswanathan and Gupta 2003; Viswanathan, Lilly et al. 2003) however the existing methodologies all use variants on either a T- or a Y- shaped reactor (Figure 1).

A major limitation of these methods is that the location of the precipitation of the metal oxide particles is not controlled and particles of metal oxide are known to precipitate in the inlet pipes. The T piece reactor would block in the metal salt inlet at least every other run, resulting in costly and inconvenient down time required for reactor cleaning and reassembly. These blockages can occur within minutes of the metal salt feed reaching the

T piece. Additionally, if the system is under pressure there are obvious health and safety implications associated with frequent blockages (i.e. increased risk of explosion). This invention consists of a novel design of reactor that is not subject to these problems.

Description of the Invention

A schematic diagram of the invention is shown in Figure 2. As previously stated, the major problem with other reactor designs is one of blockage by precipitated metal particles. This invention solves this problem by controlling the precipitation and localising it at the point of the chemical reaction. This is achieved by keeping the aqueous salt stream cold and preventing mixing or interaction of this aqueous stream until it reaches the region in which the chemical reaction occurs. An additional benefit is that the cold salt solution also acts as effective heat sink, removing the heat from the exothermic oxidation reaction.

Referring to Figure 2, the aqueous stream is introduced into the bottom of the reactor, where it is cooled, preferably by a heat sink. The solution is forced under pressure in an upwards direction. The supercritical water is introduced into the reactor in the opposite direction – i.e. downwards. The scH_2O is less dense than the aqueous stream, and thus rises upwards once inside the reaction chamber, becoming intimately mixed with the aqueous salt solution as it does so. This mixing is highly efficient, and results in the generation of metal oxide nanoparticles that can be separated downstream from the aqueous effluent.

This design takes advantage of the density differential between the two reactant streams (i.e. the scH_2O and the cold aqueous salt solution). This differential creates a strong, desirable mixing environment within the reactor and induces strong eddies downstream of the mixing point. These eddies are desirable as they help to disperse the metal oxide particles and carry them away such that they do not block the reactor.

In a preferred embodiment the reactor incorporates a funnel as shown in Figure 3. This aids the mixing of the reactants, and avoids a pulsing phenomenon associated with the mixing downstream. As the scH_2O is less dense and is therefore more buoyant than the cold solution into which it is flowing a film of scH_2O forms on the surface of the funnel. This film mixes very efficiently with the colder aqueous solution flowing past it, and this has a beneficial effect on the kinetics of the reaction between the scH_2O and the aqueous solution.

Advantages

Previous methods tend to have similar problems (e.g. blockage and lack of reproducibility). This invention represents a step-change in design, which does not obviously follow from existing knowledge.

The principle advantages of this invention are:

1. The reactor does not block. This is the main problem with other reactor configurations and is caused by back mixing in the inlets to the mixer. This causes particulate formation upstream of the mixing point and consequent flow restriction and eventual blockage of the reactor. This invention eliminates this by removing the potential for mixing to occur in the inlets of the reactor.
2. The invention allows the metal salt to remain relatively cool until mixing occurs. This has the following advantages over existing designs:
    a. No preheating of the metal salt solution occurs. This both saves on energy and removes the possibility that increasing the temperature of the salt stream will cause the metal salt to precipitate prematurely. This known to happen for certain metal salts e.g. Copper salts can precipitate out of solution if the bulk temperature of the metal salt solution is over 50-60°C. The tendency for premature precipitation depends partly on the metal salt and also it's concentration in solution.
    b. There is the potential to include a heat sink around the metal salt inlet to ensure efficient heat dissipation away from the reaction – this cannot be done using existing reactor designs as it hinders the mixing of the two streams.
    c. The rapid heating of the metal salt solution on contact with the much hotter supercritical H_2O stream instantaneously causes a multitude of nucleation sites to form. These nucleation sites are extremely small, and

act to restrict the size of the resultant particles to the desirable nanometre scale.

3. The supercritical water stream can be kept hot using a heater around the outer tube (the outlet). This is advantageous because:
    a. It allows the reactions to continue beyond the initial mixing point, thereby increasing yield.
    b. The funnel configuration allows a controlled and symmetrical mixing of the two streams. This is a marked contrast to the current state of the art, where a t-piece is commonly used to mix the two streams. It should be noted that the funnel is not an essential part of the design, since the reactor can be run with only a straight supercritical water inlet pipe. However, the funnel aids the mixing of the two solutions and allows more consistent particle size and morphology to be obtained than if the inlet is only a pipe. The t-piece favoured in the prior art did not create uniform mixing across the inlets into the mixing zone, resulting in frequent reactor blockage and consequent down time.
4. The more efficient mixing allows the production of metal oxide nanoparticles with surface areas significantly higher than previously observed. For example, ZrO_2 nanoparticles have been produced with a relatively high surface area of $200m^2/g$) This could potentially increase their catalytic activity.
5. Metal oxides that have been previously difficult to produce have been run in the reactor without blocking e.g. Ag at around $60m^2/g$. This demonstrates that a broader range of potential nanoparticulates metal based catalysts could be produced in the device than in existing designs.

Examples:

A selection of results obtained from the new reactor design is shown below.

Table 1

Metal Type	***BET surface area***	***Average Particle Size (either from XRD or surface area calculation)***
TiO_2	113 m^2/g	13nm
CeO_2	average 100m^2/g	9nm
ZrO_2	194m^2/g	6nm
ZnO	16.5 m^2/g	64 nm
CuO / Cu_2O / Cu	10 - 20 m^2/g	50nm
$Cu_{0.5}\ Zn_{0.5}\ O_2$	55m^2/g	15nm
Ag	60m^2/g	9nm

Example 1: The production of Nanoparticulate CeO_2

Reaction Scheme:

Hydrolysis: $Ce(NO_3)_4 + 4H_2O \rightarrow Ce(OH)_{4(s)} + 4HNO_3$

Dehydration: $Ce(OH)_4 \rightarrow CeO_2 + 2H_2O$

System pressure was set to 3300psi. The metal salt solution ($Ce(NO_3)_4$, (0.2 M)) was flowed at 5 ml/min through the reactor. A total of 250 ml of the metal salt solution was used during the course of the 50 min run. The scH_2O was flowed at 10 ml/min through the reactor at a temperature of 420 °C. The reactor was maintained at a temperature of 370 °C using a band heater for the duration of the reaction.

The reaction yielded yellow/white particles of CeO_2 (diameter ~9 nm, surface area 100 m^2/g) in >99% yield.

The reactor can be run for hours without blocking producing 2-5g per hour of the metal oxide. In its current configuration, the reactor has not blocked as a result of particle build up.

Example 2: Control over surface area with flow rate within the reactor

Figure 4 shows the effect of increasing flow rate of Cerium Nitrate up through the reactor. Clearly there is an interesting trend of increasing surface area (from $65m^2/g$ up to $100m^2/g$) with increasing metal salt flow up to a value of 8ml/min beyond which the particle size begins to decrease. It is possible that the increase is caused by the relationship between flow velocity and reaction kinetics and the decrease is caused by an 'excess' of metal salt resulting in larger particles being produced.

Example 3: Control over surface area with temperature within the reactor

One area of interest is the effect of the operating temperature within the reactor and it's impact on surface area. The reactor can be heated externally to any given temperature sub or super critical, the relationship between surface area (and indirectly, particle size) and operating temperature can be established. Even though the heated water inlet inside the reactor may be operating sub critical, the temperature differential between the metal salt and the heated water still exists and this will cause the inlet flow to turn upwards into the downstream outlet of the pipe, as shown in Figure 2.

Figure 5 is a graph showing how surface area increases significantly with operating temperature. This indicates that the particle size (and possibly the morphology) can be tailored by adjusting the operating conditions of the reactor.

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Hao, Y. L. and A. S. Teja (2003). "Continuous hydrothermal crystallization of alpha-Fe2O3 and Co3O4 nanoparticles." Journal of Materials Research **18**(2): 415-422.

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Viswanathan, R., G. D. Lilly, et al. (2003). "Formation of zinc oxide-titanium dioxide composite nanoparticles in supercritical water." Industrial & Engineering Chemistry Research **42**(22): 5535-5540.

Claims

1) A device capable of mixing two fluids of differing densities in which the less dense fluid is introduced into the device in a downwards orientation relative to a upwards flow of denser fluid.

2) A device as specified in Claim 1, characterised by the inlet of the less dense fluid having a conical nozzle to aid mixing of the fluids.

3) A device as specified in the preceding claims in which the denser of the two solutions is cooled prior to entry into the reactor.

4) A device in which two or more devices specified in the preceding claims are used in series.

5) A method of mixing two fluids of differing densities in the devices of the preceding claims such that the mixing is both efficient and localised within the device.

6) A method as claimed in Claim 5 in which one or both fluids is/are in the near critical or supercritical state.

7) A method as claimed in any of the preceding claims, in which one of the fluids is near-critical or supercritical water.

8) A method as claimed in any of the preceding claims, in which one of the fluids is an aqueous salt solution.

9) A method as claimed in any of the preceding claims, in which the device is used in the synthesis of metal nanoparticles.

10) A method as claimed in any of the preceding claims in which the device of Claims 1 – 4 is used to produce nano-particulate cerium oxide.

11) A method as claimed in any of the preceding claims in which the device of Claims 1 – 4 is used to produce nano-particulate titanium oxide.

12) A method as claimed in any of the preceding claims in which the device of Claims 1 – 4 is used to produce nano-particulate zirconium oxide.

13) A method as claimed in any of the preceding claims in which the device of Claims 1 – 4 is used to produce nano-particulate copper oxide.

14) A method as claimed in any of the preceding claims in which the device of Claims 1 – 4 is used to produce nano-particulate silver oxide.

15) A method as claimed in any of the preceding claims in which the device of Claims 1 – 4 is used to produce mixed metal oxides, specifically mixed copper and zinc oxides.

ABSTRACT

COUNTER CURRENT MIXING DEVICE FOR TWO DIFFERENT FLUIDS

A device for mixing efficiently two fluids of widely differing densities. In a preferred embodiment, one of the fluids is supercritical water, and the other is an aqueous salt solution. Thus, the device enables the production of metal oxide nanoparticles as a continuous process, without any risk of the reactor blocking due to the inefficient mixing inherent in existing reactor designs. Methods of obtaining various metal nanoparticles using this device are also claimed.

Figures

Figure 1: Existing T- and Y- shaped reactors

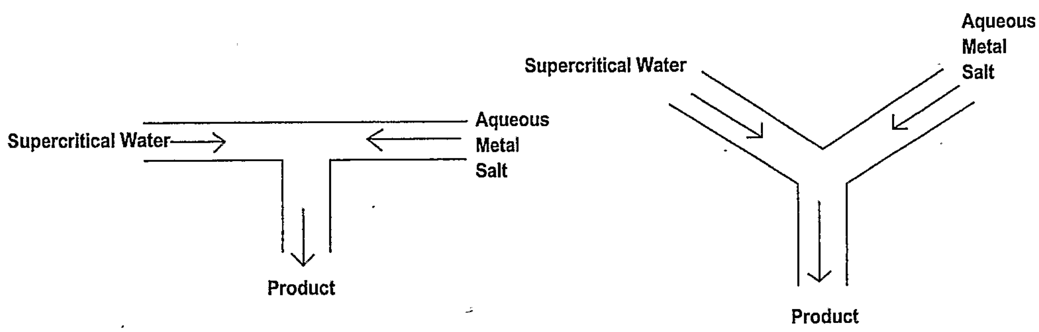


Figure 2 – A schematic of the funnel reactor geometry

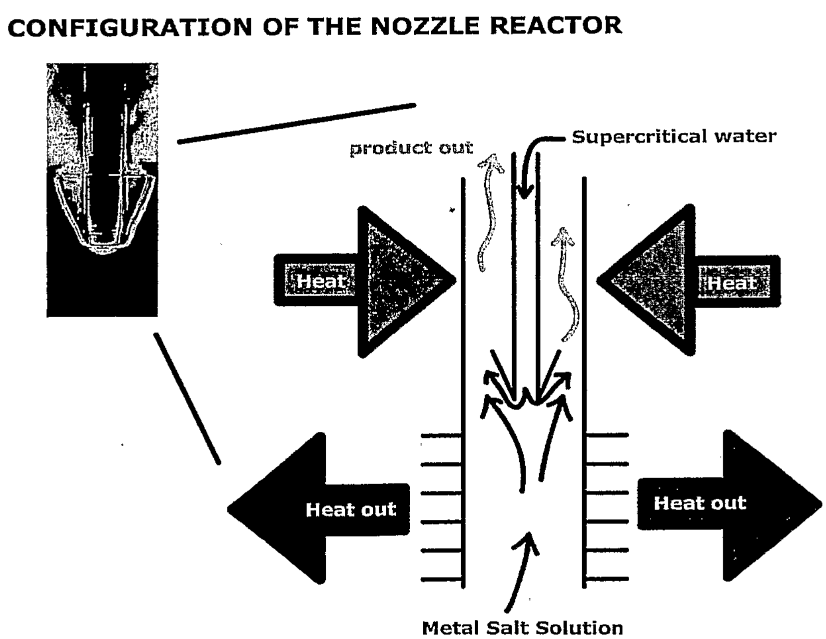


Figure 3 – A diagram of the funnel shaped supercritical outlet

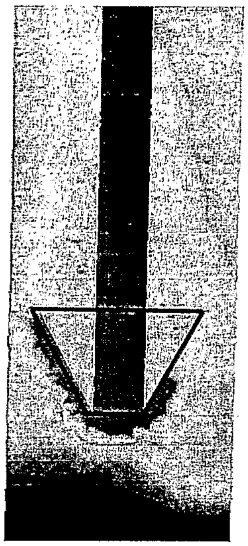


Figure 4 - The relationship between surface areas and metal salt flow rate

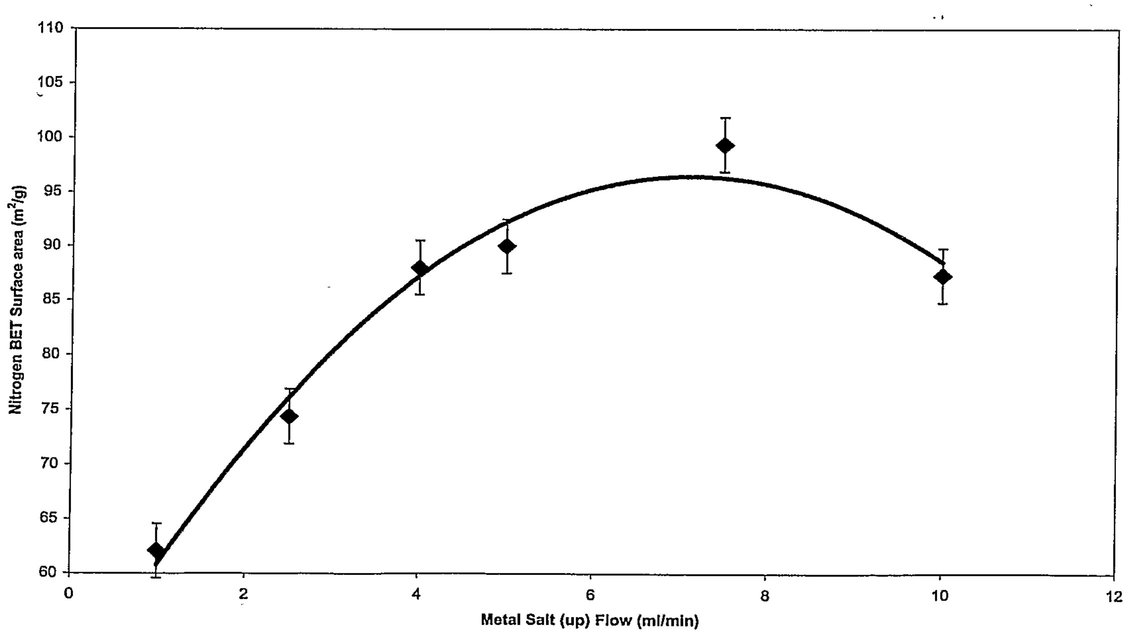
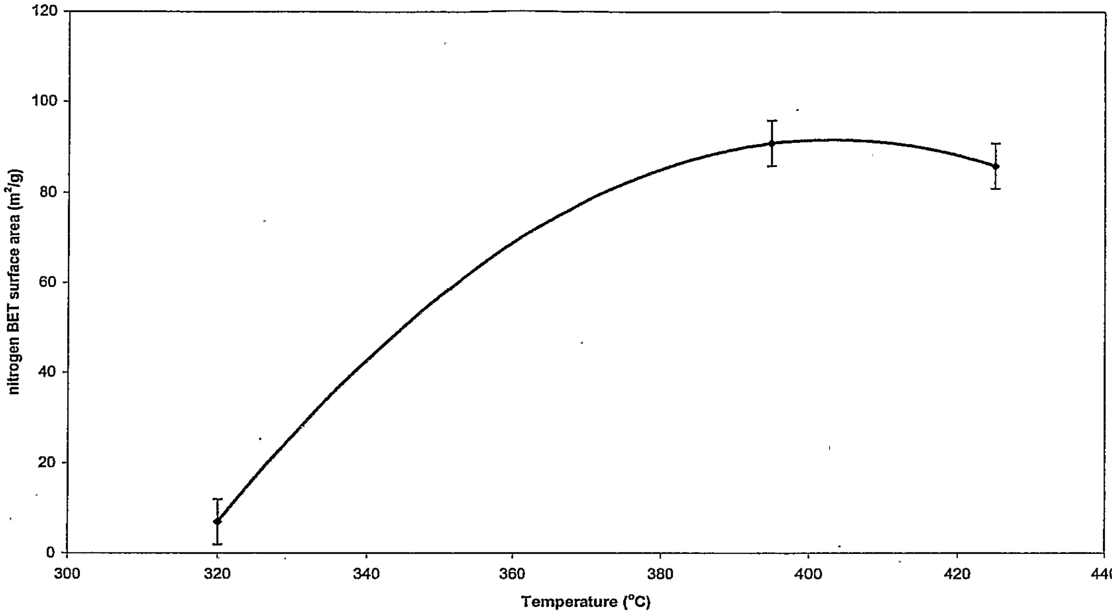


Figure 5 - The relationship between surface areas and internal reactor temperature



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